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COPYROLYSIS OF GOYNUK OIL SHALE AND THERMOPLASTICS

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ABSTRACT

In this study copyrolysis of Turkish Goynuk oil shale and polyethylene and polystyrene are investigated. The copyrolysis results are compared with the calculated values from pyrolysis results of each component. The study is aimed to find out the possible synergistic effect on the yields and compositions of the products.

Pyrolysis of polyethylene resulted in 93% conversion at 550°C without catalyst. This value is almost equal to weight loss at 550°C in TG analysis reported earlier. Pyrolysis oil contains about 92% aliphatic hydrocarbons mainly linear alkanes and alkenes (C_9-C_{34}). About 3% aromatic hydrocarbons are detected in toluene elute.

Pyrolysis of oil shale alone resulted in about 50% yield. The oil contains 33% aliphatic hydrocarbons and 14% aromatic hydrocarbons. TGA of Goynuk oil shale show that weight loss started at about 300°C and ended at about 550°C which is similar to low density polyethylene weight loss.

As expected the copyrolysis of oil shale and polyethylene gave high percentage of aliphatic structures. However, an interesting product distribution in toluene elute was observed in which the ratio of alkyl benzenes to alkyl naphthalenes changed significantly when oil shale and polyethylene copyrolyzed. This is probably due to pyrolysis product of polyethylene which can penetrate to the micro pores of oil shale easily and help in desorption and extraction of alkyl naphthalene's. During the pyrolysis at lower temperatures (≈150°C), polyethylene melts and separates as a lower phase from oil shale particles and the vapours of pyrolysis products of polyethylene pass through the oil shale particles. Besides, the alkene / alkane and alkadiene / alkene product distribution in pentane elute was also changed. As polyethylene content is decreased, the alkadiene content increased and alkene content decreased. This shows that polyethylene acts as a hydrogen donor compound.

INTRODUCTION

In the digenesis of oil shales (OS) the mineral is in a state where a small proportion of its organic content is bitumen and majority of its remaining organic content is kerogen. The usual way of extracting oil from oil shale is by heat distillation in a retort. One of the controlling parameters determining the oil yield is the stabilization of the excited volatile species to liquid products. Fractionation to smaller molecular weight compounds ending in the gaseous phase and char forming retrospective reactions especially in the presence of clay minerals are the contenders to the oil in pyrolysis processes. This effect is pronounced in self generated atmospheres, due to the long contact times of the volatiles to be catalyzed to char or heated by the hot surfaces to gases. Similar effects have been observed in coal liquefaction studies which also suffers hydrogen deficiency (Chackrabartty, S.K.,et.al.,1985). One way of preventing this shortage is to use copyrolysis operation which seems to either increase the oil yield or modify the composition of the liquid products.

(Saxby et al. , 1990.) copyrolysed a lignite and Rundle Australian oil shale and found that the addition of lignite gave a slight synergistic effect in terms of increasing the oil yield of the oil shale. In the same study it has been found that the molecular weight of the resultant oil was reduced. (Ekinci et al. 1992) conducted copyrolysis studies of Goynuk oil shale and Yatagan lignite and Seyitomer oil shale and Seyitomer lignite. Coprocessing of oil shales and lignites resulted in consistently higher oil yields. The effect is explained as oil shales preventing more of the retrospective lignite char-forming reactions. The product characterization showed that the copyrolysis products had increased alkane and aromatics and had decreased polar fractions. It is further reported that the synergistic effects disappeared in well-swept and fluidized bed reactors (Citiroglu et al. 1991).

In another Turkish oil shale and lignite coproylosis study, n-alkane distribution was used to analyse the products obtained from 1:1 and 1:2 lignite to oil shale mixtures. The Type I kerogen distribution was masked with the contributions from lignite for the former but the distribution shifted towards the Type I kerogen for the latter. The net increase in the yield due to mixture is attributed to the possible effect of water vapour arising from lignite in the mixture, catalytic effect of inorganic matrix and solvent extraction effect of the oil shale volatiles on the lignite which may involve hydrogen transfer (Okutan et al. ,1993).

(Kıran et.al, 2000) investigated the pyrolysis of waste polyethylene (PE) and polystyrene (PS) and their mixtures. The liquid yield of waste PS was found to be higher than waste PE. The dominant product of waste PS was styrene monomer followed by toluene, naphthalene and xylene, the main products of PE was polypenyl benzene followed by butenylbenzene.

EXPERIMENTAL

The Göynük A oil shale samples were collected from different locations in the excavated open-cast seams. The raw oil shale samples were crushed to 100–200 μm particle size and dried in vacuum at 40°C. Raw oil shale, plastic, and the mixtures of oil shale and plastics have been pyrolysed in a fix-bed retort. The pyrolysis experiments were conducted under a range of conditions using a modified Heinze retort. The temperature was controlled using a thermocouple inside the retort, connected to a temperature controller. 25 g sample of oil shale, plastics and mixture were used in the pyrolysis experiments. In all experimental runs, the retort was heated at 4°C/min to 550°C and held at this temperature for 60 min. The experiments were carried out in self generated (static) atmosphere.

Low density polyethylene (PE) and polystyrene (PS) granules of about 2 mm particle size were obtained from Petkim plant in Turkey. The H/C ratios of Goynuk oil shale and polyethylene and polystyrene samples were 1.5 , 2 and 1 respectively.

Collected pyrolysis oils were fractionated into pentane soluble and insoluble fractions by using 1g tar in 100 ml n-pentane. Then, the n-pentane soluble part was separated into aliphatic, aromatic and polar fractions with column adsorption chromatography using silica gel with particle size of 70-235 mesh and pentane, toluene and methanol as elution solvents. Aliphatic, aromatic and polar fractions were examined by GC-MS and FT/IR.

RESULTS AND DISCUSSION

The pyrolysis results of Goynuk oil shale (GOSh) and polyethylene (PE) and copyrolysis results of those two components are shown in Table 1 and in Figure 1.

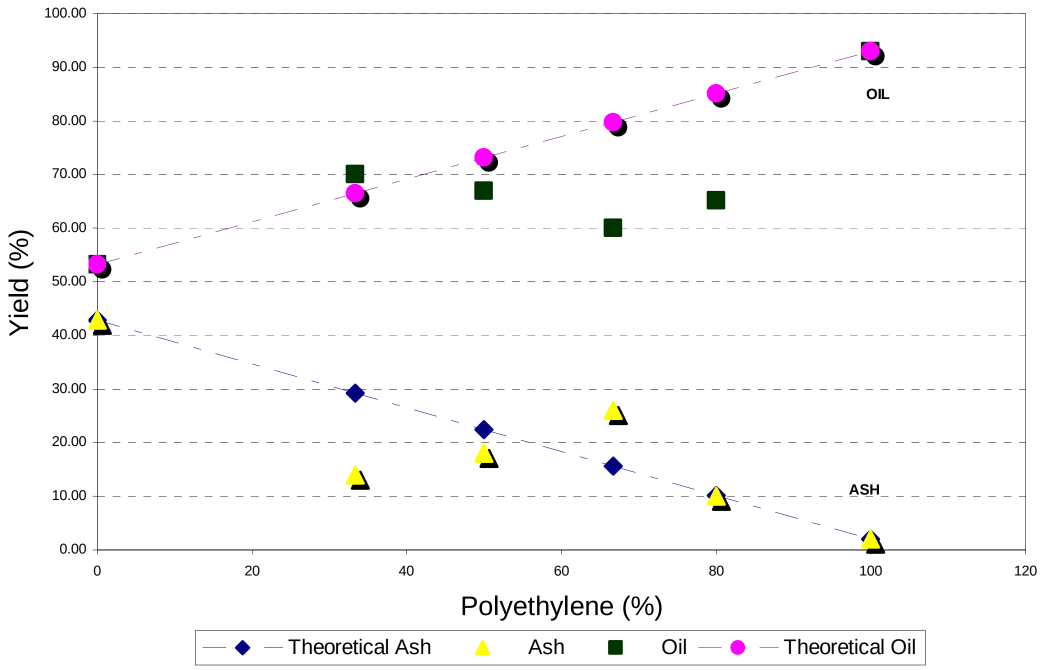
Pyrolysis of polyethylene resulted in oil yield of 93% at 550°C without catalyst. This value is almost equal to weight loss at 550°C in TG analysis reported earlier (Murty et.al. ,1996). Pyrolysis oil of PE contains about 92% aliphatic hydrocarbons mainly linear alkanes and alkenes (C_9 - C_{34}) and about 3% aromatic hydrocarbons present in toluene elute.

Pyrolysis of oil shale alone gave shale oil yield of about 50% and the oil contains 33% aliphatic hydrocarbons and 14% aromatic hydrocarbons. TGA of Goynuk oil shale show that weight loss started at about 300°C and ended at about 550°C this is similar to low density polyethylene weight loss. Generally, copyrolysis of GOSh and PE resulted in an erratic change in the oil yield compared to the calculated theoretical value. At lower PE to GOSh ratios, an increase is realized in oil yield at the expense of the ash which suggests that at these ratios char formation seems to be depressed. However, at the higher end of PE to GOSh ratio, this trend is lost and calculated ash content is higher or about the same as the copyrolysis results. From these results it is obvious that there is not a distinctive synergism obtained from the copyrolysis of GOSh and PE.

Table 1. The Pyrolysis Results of GOSh and PE

Code	Ratio of PE/ GOSh	PE (%)	Theoretical Ash (%)	Ash (%)	Oil Yield (%)	Theoretical Oil Yield (%)
M-001	0/1	0	42,8	42,8	53,2	53,2
M-012	1/2	33,3	29,2	14,0	70,0	66,5
M-013	1/1	50	22,4	18,0	67,0	73,1
M-014	2/1	66,7	15,6	26,0	60,0	79,7
M-015	4/1	80	10,2	10,0	65,2	85,0
M-016	1/0	100	2,0	2,0	93,0	93,0

Figure 1. Ash and Oil Yields of PE and GOSh Copyrolysis



The copyrolysis results of GOSh and Polstyrene (PS) are shown in Table 2 and in Figure 2. The copyrolysis of polystyrene and shale oil showed generally similar behaviour to the polyethylene and shale oil in the lower PS to GOSh ratios. With increasing the ratio of PS/GOSh results in an increase in the oil yield and a decrease in the total ash content. At the middle range ratios, the oil yield decreased. At the higher PS to GOSh ratios again an increase in the actual yield compared to calculated value is obtained.

One of the most striking results of the copyrolysis of GOSh and PS is that the pentane soluble fractions of produced oil have increased from 70% to above 97%. This is a significant improvement in term of quality of shale oil as refinery input and chemical feed stock.

Pentane elute of pentane soluble part of the oil product is a mixture of n-alkane and n-alkenes similar to the pentane elute of shale oil. However the toluene elute consists of about 75% styrene, 12% ethyl benzene, 3% 1-phenyl propene for the mixture of GOSh to PS : 1/1 ratio. This trend is similar to the other ratios studied in this work.

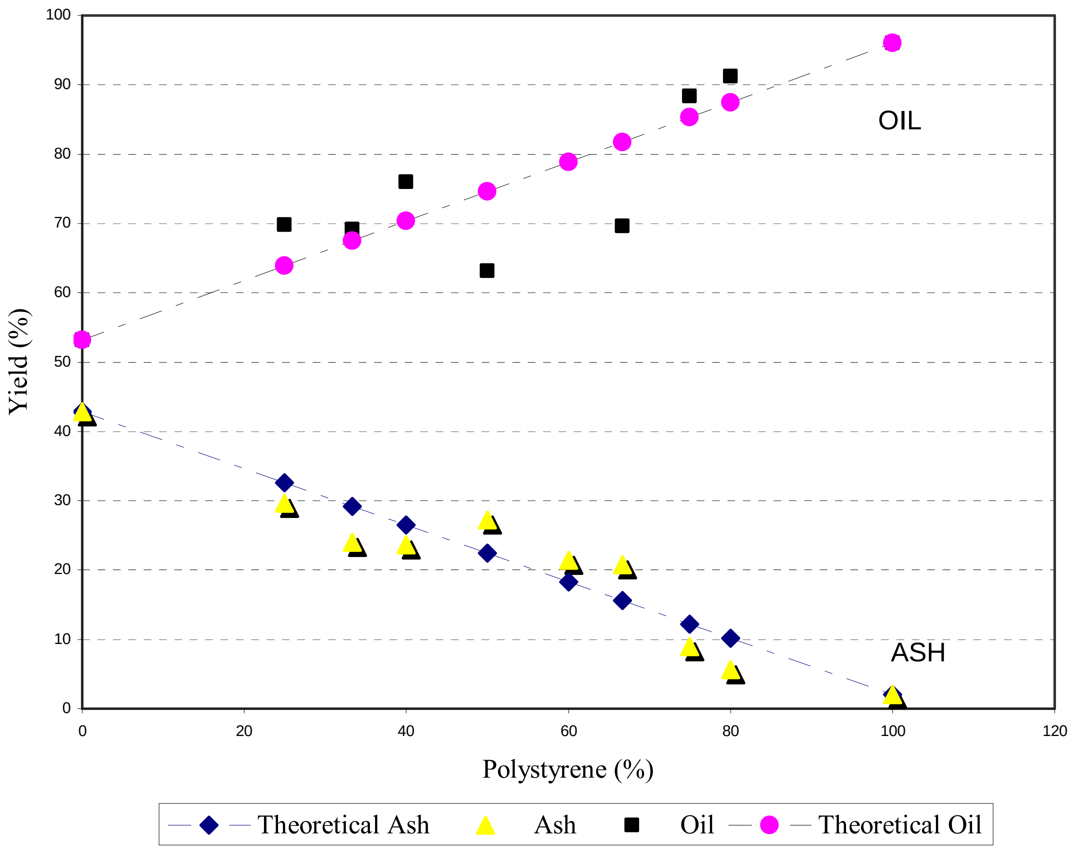
As expected the copyrolysis of oil shale and polyethylene gave high percentage of aliphatic structures. However, an interesting product distribution in toluene elute was observed. The ratio of alkyl benzenes to alkyl naphthalene's changed significantly when oil shale and polyethylene were copyrolysed. This is probably due to pyrolysis product of poly ethylene that can penetrate in the microspores of oil shale easily and help in the desorption and extraction of alkyl naphthalene.

Table 2. The Pyrolysis Results of GOSh and PS

Code	Ratio of PS/ GOSh	PS (%)	Theoretical Ash (%)	Ash (%)	Oil Yield (%)	Theoretical Oil Yield (%)
M-001	1/0	0	42,8	42,8	53,2	53,2
M-002	3/1	25	32,6	29,6	69,8	63,9
M-003	2/1	33,3	29,2	24,0	69,2	67,5
M-004	3/2	40	26,5	23,6	76,0	70,3
M-005	1/1	50	22,4	27,2	63,2	74,6
M-006	2/3	60	18,3	21,4	68.1	78,9
M-007	1/2	66,7	15,6	20,8	69,6	81,7
M-008	1/3	75	12,2	9,0	88,4	85,3
M-009	1/4	80	10,2	5,6	91,2	87,4
M-010	0/1	100	2	2	96	96,0

In Table 3 the alkene / alkane and alkadiene / alkyne product distribution in pentane elute of the GOSh and PE copyrolysis oils are compiled. As polyethylene content is decreased, the alkadiene content increased and alkene content decreased. This may indicate that polyethylene may act as hydrogen donor compound during pyrolysis.

Figure 2. Ash and Oil yields of PS and GOSh Copyrolysis



As shown in Table 4, pentane soluble part of the GOSh/PS copyrolysis oil fractionates into 38-42 % pentane, 21-30% toluene and 28-41% methanol elutes, This result is in general agreement with the literature results in which the product distribution is enriched in aliphatic and aromatic compounds at the expense of polar compounds (Saxby et al. , 1990. Citiroglu et al.1991, Ekinci et al. 1992). However the pentane elutes are found to contain some aromatic compounds using the standard shale oil fractionation procedure (Pütün, et.al.1988).

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Table 3. Alkadiene /alkine and alkenes /alkane product distribution in pentane

	Alkadiene/Alkene Ratio					Alkene / Alkane Ratio				
	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_9	C_{10}	C_{11}	C_{12}	C_{13}
GOSh	0.14	0.11	0.10	0.13		1.6	2.3	1.9	1.8	1.6
PE	0.17	0.15	0.12	0.15		1.2	1.4	1.5	1.4	1.4
GOSh / PE (2:1)	0.15	0.33	0.27	0.3	0.34	1.1	2.0	1.8	1.75	1.7
GOSh / PE (1:1)	0.16	0.13	0.14	0.16		1.8	3.4	2.2	2.4	1.9
GOSh / PE (1:2)	0.23	0.16	0.16	0.18	0.23	1.6	3.3	2.0	1.8	1.8

Table 4. Yield and Product Distribution of Copyrolysis Oil of GOSh and PS

GOSh /PS	1/0	4/1	3/1	2/1	1/1	1/2	1/3	1/4	0/1
Oil (%)	53	76	71	89	90	98	90	95	96
Theoretical oil (%)	---	59	61	66	74	82	84	88	---
Retort Residue (%)	43	22	29	10	7	1	5	4	2
Pentane soluble (%)	70	99	99	99	98	99	99	98	100
Pentane Elute (%)	33	-	-	38	41	-	42	-	25
Toluene Elute (%)	14	-	-	21	21	-	30	-	70
Methanol Elute (%)	53	-	-	41	38	-	28	-	5

CONCLUSIONS

Copyrolysis of GOSh and PE and GOSh and PS resulted in not a significant and continuous synergism at all ratios of plastics addition. However, copyrolysis resulted in distinctive effect on the composition of products. Copyrolysis of oil shale and polyethylene gave high percentage of aliphatic structures. In the toluene elute the ratio of alkyl benzenes to alkyl naphthalenes and in the pentane elute the alkene / alkane and alkadiene / alkene product distribution changed significantly as a result of copyrolysis. On the other hand, the GOSh and PS copyrolysis oils have very high pentane soluble fractions above 98%. This is a significant improvement in term of quality of shale oil in terms of refinery input and chemical feedstock. The toluene elute of GOSh and PS (1/1 ratio) copyrolysis oil was found to be consists of about 75% styrene, 12% ethyl benzene, 3% 1-phenyl propene.

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